

減圧とし、15分以内に0.5mmHgの絶対圧とし、更に15分反応せしめたところ酸化度100~105での起明のイミドエステル化合物が得られた。

特許出願人 有限会社
代理人 弁護士 岡田 純 博

特開昭53-40760(5)
手続補正書

特許庁長官殿

昭和51年11月2日

1. 事件の表示

特開昭51-115565号

2. 発明の名称

不飽和イミドエステル類の製造法

3. 補正をする者

事件との関係 特許出願人

(300) 有限会社

代表者 大 蔵 善 三

4. 代理人 東京都千代田区内幸町2丁目1番1号

(坂野ビル)

有限会社 社内

(7726) 弁護士 岡田 純 博

5. 補正の対象

明細書の「発明の形態を説明」の欄

6. 補正の内容

特許

(1) 明細書第6頁第3行目の「イノ安息香酸、
Δ5-」を「イノ安息香酸、P-アミノ安息
香酸、Δ5-」に訂正する。

以 上

2650215 — 524/262

~~2890201~~ —
260 526/262

2500738 — 525/411

~~2971944~~ — 526/256

~~3074915~~ — 526/254

3429713 — 528-319

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 267 695
A2**

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 87309135.9

(51) Int. Cl.⁴ **C08K 5/00 , C08L 23/02 ,
/(C08K5/00,5:09,5:17)**

(22) Date of filing: 15.10.87

The title of the invention has been amended
(Guidelines for Examination in the EPO, A-III,
7.3).

(30) Priority: 11.11.86 GB 8626875
23.01.87 GB 8701514

(43) Date of publication of application:
18.05.88 Bulletin 88/20

(84) Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

(71) Applicant: **IMPERIAL CHEMICAL INDUSTRIES
PLC**
Imperial Chemical House Millbank
London SW1P 3JF(GB)

(72) Inventor: **Trotolr, Jean-Paul**
236 rue des Bruyères
B-5043 Waret-la-Chaussée(BE)
Inventor: **Bath, Colin**
1 East View Summerseat
Bury Lancashire BL9 5PG(GB)

(74) Representative: **James, David Gomer et al**
Imperial Chemical Industries PLC Legal
Department: Patents Po Box 6 Bessemer
Road
Welwyn Garden City Herts, AL7 1HD(GB)

(54) **Composition comprising a carboxylic acid and an amine.**

(57) A composition comprises (a) a carboxylic acid compound which contains at least three carbon atoms and (b) an amine such as an ethoxylated amine. The composition may be obtained by conventional powder blending or melt blending techniques. The composition can be incorporated into an olefin polymer to give a polymer composition which has an increased crystallisation temperature and/or improved optical properties.

EP 0 267 695 A2

COMPOSITION

The present invention relates to compositions, more particularly to compositions comprising additive mixtures suitable for incorporation into polymer materials, the production of polymer compositions and shaped articles formed from such compositions.

Olefin polymers are readily available and widely used polymeric materials. The most extensively available olefin polymers are ethylene and propylene polymers, the term "polymer" being used to include copolymers. Propylene polymers have a melting point which is generally higher than that of ethylene polymers and hence propylene polymers are suitable for use at somewhat higher temperatures than ethylene polymers. Ethylene and propylene polymers can be used for packaging but moulded articles formed from these polymers generally show a high percentage of haze and hence are not satisfactory for applications in which good clarity is desirable.

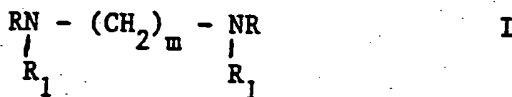
It is known that the addition of nucleating agents, for example sodium benzoate, to olefin polymers provides an increase in the crystallisation temperature, and/or an improvement in the optical properties of the polymer. Furthermore, the use of nucleating agents can allow a shorter cycle time, and hence better productivity, in an injection moulding process. However, the use of such nucleating agents is often limited due to their high price, for example dibenzylidene sorbitol, or to dispersion problems, for example with sodium benzoate.

We have now found that mixtures of certain readily available materials are effective in increasing the crystallisation temperature, and/or improving the optical properties, of olefin polymers.

According to the present invention there is provided a composition comprising (a) a carboxylic acid compound which contains at least three carbon atoms; and (b) an amine.

The carboxylic acid compound is preferably one containing at least two carboxylic acid groups attached to an optionally substituted saturated aliphatic hydrocarbon group or one containing at least one carboxylic acid group attached to an optionally substituted ring system. Carboxylic acids containing at least two carboxylic acid groups attached to an aliphatic hydrocarbon group include glutaric acid, adipic acid, succinic acid, suberic acid, pimelic acid, azelaic acid and sebacic acid. Preferred carboxylic acids of this type contain two carboxylic acid groups and from three to ten carbon atoms. Carboxylic acids containing at least one carboxylic acid group attached to a ring system include monocarboxylic acids such as benzoic acid, toluic acid, and p-tertiary butyl benzoic acid, hydroxycarboxylic acids such as salicylic acid, and dicarboxylic acids such as phthalic acid, terephthalic acid, cyclohexane-1,2-dicarboxylic acid and cyclohexane-1,4-dicarboxylic acid.

The amine which is component (b) may be a diamine or a substituted amine, for example an ethoxylated amine. Thus component (b) may be a compound of general formula I or II:



wherein:

R is a hydrocarbyl group or a substituted hydrocarbyl group and is preferably a hydrocarbyl group containing at least four carbon atoms;

R₁ is a hydrocarbyl group, a substituted hydrocarbyl group or a group (R₃O)_x(C₂H₄O)_nH;

R₂ is a hydrocarbyl group, a substituted hydrocarbyl group or a group (R₃O)_x(C₂H₄O)_nH, and may be the same as, or different from, R₁;

R₃ is an alkylene group containing 3 to 5 carbon atoms;

m is an integer and has a value of 1 to 10;

n is zero or is an integer which has a value of from 1 to 50;

and

x is zero or is an integer which has a value of from 1 to 50.

Useful mixtures have been obtained in which the amine is a compound of formula II wherein at least one of the groups R_1 and R_2 is a group $(R_3O)_x(C_2H_4O)_nH$ in which the value of n and/or x is from 1 to 50. A mixture of compounds may be used as component (b), for example a mixture of compounds in which the value of at least one of m , n and x differs. The mixture may be of compounds in which the nature of R varies, for example when R is a mixture of alkyl groups. If a mixture of compounds is used, such a mixture may be one of compounds of formula II in which there is present at least one group $(R_3O)_x(C_2H_4O)_nH$ in which group the value of n and/or x varies, and particularly at least one group in which x is zero and the value of n varies.

The group R is preferably an alkyl group and particularly is an alkyl group containing at least 8 carbon atoms. Typically R does not contain more than 20 carbon atoms.

In the compound of formula I, R_1 is preferably either a hydrogen atom [when the values of n and x are zero in the group $(R_3O)_x(C_2H_4O)_nH$], or is a methyl group or hydroxyethyl group. The value of m is preferably from 2 to 6.

In the compound of formula II, the groups R_1 and R_2 are each, independently, either a group R or a group $(R_3O)_x(C_2H_4O)_nH$ in which the value of x is zero and n is 0 to 50. Preferably the groups R_1 and R_2 are both the same as the group R or at least one of R_1 and R_2 is a group $(R_3O)_x(C_2H_4O)_nH$ in which the value of n is 1 to 50. Preferred amines are those in which at least one of the groups R , R_1 and R_2 is an alkyl group containing at least 8 carbon atoms, especially at least 12 carbon atoms. The group R_3 is preferably a propylene group. Both n and x can be zero or at least one of n and x has a positive value. The value of n and x preferably does not exceed 20 and especially does not exceed 15. The group $(R_3O)_x(C_2H_4O)_nH$ may be an OH ended alkylene oxide, for example a propylene oxide, group, an OH ended ethylene oxide group or may contain both alkylene oxide and ethylene oxide groups. If n and x both have a positive value, it is generally preferred that $(n + x)$ has a value of 2 to 50, and preferably does not exceed 20 and especially does not exceed 15.

If the acid or amine contains a substituted group, the substituent may be a hydroxy group, one or more halogen atoms, a nitrile group, a hydrocarbyloxy group, a hydrocarbonyl group such as an acyl group, a hydrocarbyloxycarbonyl or a hydrocarbonyloxy group, whereof the hydrocarbonyl groups may be further substituted with substituent groups of the foregoing types.

Amines which may be used in the compositions of the present invention include

- N,N-bis(hydroxyethyl)alkyl(C_{13} to C_{15}) amine;
- N-methyl-N-hydroxyethyl-alkyl(C_{13} to C_{15})amine;
- N,N-dimethyl-octadecylamine;
- N,N-bis(hydroxyethyl)-octadecylamine;
- N-methyl-N,N-bis(coco)amine;
- N,N-dimethyl-tallowamine; and
- N-tallow-N,N',N'-tris(hydroxyethyl)-1,3-diaminopropane.

The molar proportions of (a) and (b) can be varied widely, for example from 10:1 to 1:10. However, we generally prefer to avoid a large excess of one component relative to the other component and hence we generally prefer that the molar proportions of (a) and (b) are from 10:1 to 1:3 particularly 10:1 to 1:1. If component (a) is a dicarboxylic acid or component (b) is a diamine, the components may be used in essentially stoichiometric proportions, for example one mole of a dicarboxylic acid to two moles of a monoamine.

The composition of the present invention may be incorporated into an olefin polymer.

Thus, as a further aspect of the present invention there is provided a polymer composition which comprises an olefin polymer, a carboxylic acid compound which contains at least three carbon atoms and an amine.

The carboxylic acid compound and the amine are components (a) and (b) of the composition discussed hereinbefore.

In the polymer composition the proportion of the carboxylic acid compound is typically from 0.05% up to 3%, and preferably from 0.1 up to 1%, by weight relative to the polymer, and the proportion of the amine is typically from 0.05 up to 3%, and preferably from 0.1 up to 1.5%, by weight relative to the polymer.

The olefin polymer (which term is used herein to include both homopolymers and copolymers) may be any ethylene homopolymer or copolymer, particularly high density polyethylene or linear low density polyethylene which is a copolymer of ethylene with a higher olefin monomer such as butene-1, hexene-1, octene-1 or 4-methylpentene-1. Alternatively, the olefin polymer may be a propylene homopolymer or copolymer, for example a random copolymer of propylene with up to 8% by weight, relative to the polymer, of ethylene, or a sequential polymer obtained by polymerising propylene in the essential absence of other monomers and thereafter copolymerising a mixture of ethylene and propylene to give a polymer containing

from 5 up to 30% by weight of ethylene.

The polymer composition may be obtained by adding the carboxylic acid and the amine separately to the olefin polymer or the acid and the amine may be pre-mixed and then added to the olefin polymer. The acid and the amine when incorporated into an olefin polymer, result in an increase in the crystallisation temperature and/or an improvement in optical properties of the polymer. The acid and amine which are used in the composition of the first aspect of the present invention can react together and we have found that the reaction product is less effective in giving the desired effects when incorporated into an olefin polymer. Accordingly, we prefer to avoid maintaining these compositions at an elevated temperature, for example above 120°C and especially above 200°C, for a prolonged period of time, for example in excess of 15 minutes.

Some components of the compositions of the first aspect of the present invention are either liquids or waxy solids at ambient temperature and are difficult to handle in this form, especially if accurate metering of the components is required. Hence, it may be preferred that the compositions are obtained as a polymer masterbatch containing a higher concentration of the composition than is required in the final polymer composition. The polymer masterbatch may be a mixture obtained by blending, without melting, with a particulate polymer. However, it is generally preferred that the masterbatch has been obtained by blending with molten polymer, and in this case it is particularly preferred that component (a) and component (b) are formed into separate masterbatches to minimise reaction between components (a) and (b). The amount of additive in the masterbatch is dependent on the nature of the particular additive. Typically the masterbatch contains at least 5% by weight of additive but in general the level of additive does not exceed 50% by weight. A convenient level of additive in the masterbatch is 10 to 15% by weight. If components (a) and (b) have been formed into separate masterbatches, these may be pre-mixed in any desired proportion and the mixture may be added to a polymer. Alternatively, the separate masterbatches may be added separately to the polymer, without being premixed. We have found that with some amines, the use of a masterbatch not only results in easier handling of the material but can also lead to improved colour in the final polymer composition.

If a polymer masterbatch is formed, it will be appreciated that it is desirable that the polymer used to form the masterbatch should be compatible with the polymer used for the polymer composition. Thus, the polymer used for the masterbatch is preferably of the same general type as the polymer used for the polymer composition, for example both polymers are low density polyethylene or are both propylene homopolymers. In general the amount of masterbatch to be used is a minor proportion of the final polymer composition and compatibility may be more readily achieved using such relative proportions of the polymers. Typically the masterbatch is used in an amount of 1 to 10% by weight of the final composition when using a masterbatch containing 10% by weight of the acid and/or amine. Conveniently there is used 1 to 6% by weight of an amine masterbatch containing 10% by weight of amine and 3 to 5% by weight of an acid masterbatch containing 10% by weight of acid. Masterbatches containing other proportions of additive are added in the appropriate amounts in dependence on the level of additive in the masterbatch and the level required in the final polymer composition.

The polymer compositions of the present invention possess an increased crystallisation temperature and/or improved optical properties compared to the original polymer. We have found that if the olefin polymer is a linear low density polyethylene, the incorporation of the carboxylic acid and the amine, in addition to giving improvements in optical properties and/or crystallisation temperature, can also result in improved gloss.

The polymer composition of the present invention may also include other additives which are conventionally added to olefin polymers. Thus, the polymer composition may include other nucleating agents and we have observed further improvements in crystallisation temperature and/or in optical properties in compositions containing finely divided silica in proportions of less than 1% by weight relative to the polymer. By finely divided silica is meant silica having an average particle size of not more than 5 micrometres and especially not more than one micrometre.

The polymer composition also typically includes additives to at least partially inhibit the degradation of the olefin polymer component of the composition. These additives include, inter alia, antioxidants, light stabilisers, antacids, lubricants and, as necessary, copper or metal deactivators. The proportion of each of such additives is typically less than 2% by weight based on the olefin polymer and in general does not exceed 1% by weight based on the olefin polymer. A wide range of additives which provide some inhibition of the degradation of olefin polymers are known and the skilled worker will be able to select appropriate additives in accordance with the particular olefin polymer and the conditions under which it is to be processed and used. Examples of additives which can be used include, inter alia, 1,1,3-tris(2-methyl-4-hydroxy-5-tertiarybutylphenyl)butane in combination with dilaurylthiodipropionate;

- polymerised 1,2-dihydro-2,2,4-trimethylquinoline;
 2,6-di-tertiarybutyl-4-methylphenol;
 4,4-thio-bis-(6-tertiarybutyl-4-methylphenol);
 oxalic acid bis (benzylidene hydrazide);
 5 N,N'-bis(beta-3,5-ditertiarybutyl-4-hydroxyphenyl)propiono) hydrazide;
 pentaerythritol-tetra-[3-(3,5-di-tertiary-butyl-4-hydroxyphenyl)propionate];
 beta-(3,5-di-tertiary-butyl-4-hydroxyphenyl)-propionic acid-n-octadecyl ester;
 2,2-bis[4-(2-(3(3,5-di-tertiary-butyl-4-hydroxyphenyl)propionyl) oxy)ethoxy)phenyl]propane;
 2-(2'-hydroxyphenyl)-benzotriazole derivatives;
 10 2-hydroxybenzophenones such as 4-octoxy-2-hydroxybenzophenone;
 sterically hindered amines such as 4-benzoyl-2,2,6,6-tetramethylpiperidine;
 tris(2,4-di-tertiary-butylphenyl)phosphite;
 calcium stearate;
 zinc stearate; and
 15 dehydrotalcite.

The polymeric compositions in accordance with the present invention may be formed into film and other shaped articles by any suitable technique, particularly by extrusion or, especially, by injection moulding. We have found that the effectiveness of the composition of a carboxylic acid and an amine can be dependent to some extent on the technique used to obtain the shaped article. Particularly useful effects
 20 have been noted when the shaped article has been obtained by injection moulding.

The composition of the present invention, and the polymer composition, may be obtained by blending the components of the composition together using any known, suitable technique as discussed previously herein. The polymer, carboxylic acid and amine may be mixed under conditions in which the polymer is molten, the mixture granulated and the granulated polymer used in a subsequent melt processing stage to
 25 give a shaped article, particularly by injection moulding. However, in order to minimise the time during which the acid and amine are mixed at elevated temperature, it is preferred that the acid and amine are added separately, or as a mixture obtained by a solids blending technique, to the polymer at the final stage of producing a shaped polymer article, for example at the injection moulding stage.

The production of compositions and polymer compositions in accordance with the present invention are
 30 described in the following illustrative examples, in which some properties of the compositions produced are also given. Unless otherwise stated, percentages in the polymer composition are by weight relative to the polymer component.

35 Examples 1 to 4

Compositions were prepared by blending the components together on a two roll mill, the front roll being at 190°C and the back roll being at 150°C. The polymer was added first and worked until melting occurred. The additives were then added to the mill and working was continued until the additives were completely
 40 homogenised (this required 10 to 15 minutes from the initial addition of the polymer) and there was no evidence of particle agglomeration, as indicated by white specks in the crepe. The milled composition was granulated using a Pallman granulator.

The granules were used to obtain a blown film by means of a Brabender 8266-25D extruder having a 1.9 cm diameter screw having a length:diameter ratio of 25:1. The screw was operated at 45 r.p.m. and the
 45 temperature profile in the extruder to the die was 230°C, 240°C, 250°C and 260°C (at the die). The polymer was extruded through an annular die gap of diameter 2.64 cm and width of 1 mm. The extruded tube was blown, by air pressure, to a blown film of diameter about 15 cm and having an average film thickness of 60 micrometres.

The crystallisation temperature was determined by cooling a sample of the molten polymer composition
 50 at a rate of 20°C per minute using a Perkin-Elmer Differential Scanning Calorimeter. Percentage haze was determined in accordance with ASTM Test Method D 1003-59T using an "EEL" Spherical Haze Meter.

The results obtained are set out in Table 1, together with the results of comparative examples not in accordance with the present invention.

Table 1

	Example or Comp.Ex.	Polymer (a)	Additives		Crys.temp (d)		Haze (%) (e)
			Type (b)	Weight (%) (c)	Start (°C)	Peak (°C)	
5							
10	A	I	N11	N11	111.5	107	68
	B	I	SiO ₂	0.1	119	114	39
	C	I	A	0.5	117	108.5	57
15	D	I	AA	0.3	124.5	119.5	24
	E	I	AA	0.5	123.5	119.5	30
20	I	I	(A (AA	(2.0) (0.5)	122	117.5	22
	2	I	(A (AA (SiO ₂	(2.0) (0.5) (0.1)	126	122	22
25							
	F	I	GA	0.3	128	122.5	20
	G	II	N11	N11	112	106.5	61
30	H	II	A	2.0	107	103.5	52
	I	II	AA	0.3	126	121	15
35	J	II	AA	0.5	129	125	18
	3	II	(A (AA	(2.0) (0.5)	125.5	121.5	26
40	4	II	(A (AA (SiO ₂	(2.0) (0.5) (0.1)	128.5	125	16
	K	II	GA	0.3	129	126	12
45							

Notes to Table 1

(a) I is propylene homopolymer "Propathene" (Registered Trade Mark) grade GWE 26, available from Imperial Chemical Industries PLC.

II is propylene homopolymer Novolen grade 1100 LX, available from BASF AG.

(b) SiO₂ is a finely divided hydrophobic silica, Sipernat 50S, available from Degussa AG.

A is an ethoxylated amine of the type RN[(C₂H₄O)_nH]₂ where n has a value of one and R is a mixture of linear and branched aliphatic groups containing from 13 to 15 carbon atoms.

AA is adipic acid.

GA is glutaric acid.

(c) % weight is weight of additive relative to the polymer.

(d) Crystallisation temperature is as determined by differential scanning calorimetry using a cooling rate of 20°C/minute.

(e) % haze is as determined in accordance with ASTM Test Method D 1003-59T and is measured on a sample of the film formed.

Examples 5 and 6

The procedure of Examples 1 to 4 was repeated using two different linear low density polyethylenes and different additives, the processing conditions being the same.

The results obtained are set out in Table 2, together with the results of comparative examples not in accordance with the present invention.

Table 2

<u>Example or Comp.Ex.</u>	<u>Polymer (f)</u>	<u>Additives</u>		<u>Haze (%) (e)</u>	<u>Gloss (%) (i)</u>
		<u>Type (b) (h)</u>	<u>Weight (%) (c)</u>		
L	III	N11	N11	22	41
M	III	LD	15	14	66
5	III	(LD (A (AA	(1 (0.1 (0.5)	10	78
N	IV	N11	N11	34	20
O	IV	LD	15	22	63
6	IV	(LD (A (AA	(15 (0.1 (0.5)	13	65

Notes to Table 2

(b), (c) and (e) are all as defined in Notes to Table 1.

(f) III is a linear low density polyethylene available from Essochem as grade LL 1201.

5 IV is a linear low density polyethylene available from Essochem as grade LL 1417.

(h) LD is low density polyethylene and is available from Essochem as LD 183.

(i) % gloss is as determined on a sample of the film formed using the procedure of British Standard 2782, Method 515B.

10

Examples 7 to 10

Further compositions were produced by the procedure of Examples 1 to 4 and the results are given in Table 3.

15

Table 3

20	<u>Example or Comp.Ex.</u>	<u>Polymer (j)</u>	<u>Additives</u>		<u>Crys.temp (d)</u>		<u>Haze (%) (e)</u>
			<u>Type (b)</u>	<u>Weight (%) (c)</u>	<u>Start (°C)</u>	<u>Peak (°C)</u>	
	P	V	Nil	Nil	110.5	106	67
25	Q	V	A	2.0	113	106.5	46
	7	V	(A (AA	0.1) 0.5)	120.5	114	43
30	8	V	(A (AA	2.0) 0.5)	118.5	113.5	38
	R	VI	Nil	Nil	113	106.5	78
35	S	VI	A	2.0	112.5	106.5	72
	9	VI	(A (AA	0.1) 0.5)	127.5	122	69
40	10	VI	(A (AA	2.0) 0.5)	127	124.5	69

45 Notes to Table 3

(b), (c), (d) and (e) are all as defined in Notes to Table 1.

(j) V is propylene homopolymer, 'Propathene' (Registered Trade Mark) grade GWM 22, available from Imperial Chemical Industries PLC.

50 VI is propylene copolymer, 'Propathene' (Registered Trade Mark) grade GWM 101, available from Imperial Chemical Industries PLC.

Examples 11 to 18

55

Further compositions were prepared and tested as follows.

The additives were mixed with particulate polymer by tumble-blending and extruding the powder blend using a Betol extruder having a 25 mm diameter screw with a cavity transfer mixer. The temperature profile

in the extruder was 190°C up to 220°C, dropping to 205°C at the die. The extruded lace was passed through a water bath, dried and then granulated.

The products obtained were then formed into discs of 8.9cm diameter and 1.6mm thickness by injection moulding the granules using a Boy 30M injection moulding machine operating at 240°C and with a mould temperature of 50°C. On ejection from the mould, the moulded discs were allowed to cool naturally.

Haze measurements were effected on the injection moulded discs using a Gardner Hazemeter.

The polymer used was a random copolymer of propylene and ethylene containing about 2.6% weight of ethylene and available as 'Propathene' (Registered Trade Mark) grade PXC 22406 from Imperial Chemical Industries PLC.

The results obtained are set out in Table 4, together with the results of comparative examples not in accordance with the present invention.

Table 4

	<u>Example or Comp.Ex.</u>	<u>Additives</u>		<u>Cryst. temp. peak (°C) (1)</u>	<u>Haze (%) (m)</u>
		<u>Type (b) (k)</u>	<u>Weight (%) (c)</u>		
20	T	N11	N11	104.5	71
	U	A	0.5	ND	88
25	V	A	1.0	ND	84
	W	TBA	0.35	124	37
	II	TBA A	(0.35) (0.54)	126	20.5
30	X	BA	0.35	124	67
	12	BA A	(0.35) (0.78)	125.5	27
35	Y	AA	0.35	123	58
	13	AA A	(0.35) (0.66)	123.5	44
40	14	AA A	(0.35) (1.31)	123.5	41
45	Z	C12	0.35	115	83
	15	C12 A	(0.35) (0.56)	120.5	45
50	16	C12 A	(0.35) (1.11)	120.5	45
	17	C14 A	(0.35) (0.56)	121	49
55	18	C14 A	(0.35) (1.11)	121.5	47

Notes to Table 4

(b) and (c) are both as defined in Notes to Table 1.

(k) TBA is p-tertiarybutylbenzoic acid.

5 BA is benzoic acid.

C12 is cyclohexane-1,2-dicarboxylic acid.

C14 is cyclohexane-1,4-dicarboxylic acid.

(l) As determined by differential scanning calorimetry and is the temperature of the highest rate of crystallisation on cooling from the melt at 20°C/minute.

10 (m) % haze is determined in accordance with ASTM Test Method D 1003-59T using a Gardner Hazemeter and is measured on an injection moulded disc.

ND means Not Determined.

15 Examples 19 to 25

The procedure described for Examples 11 to 18 was repeated with the exception that the polymer used was a different random copolymer containing about 3% weight of ethylene and available as 'Propathene' (Registered Trade Mark) grade PXC 22265 from Imperial Chemical Industries PLC.

20 The results obtained are set out in Table 5, together with the results of comparative examples not in accordance with the present invention.

25

30

35

40

45

50

55

Table 5

	Example or Comp. Ex.	Additives		Cryst. temp. peak (°C) (l)	Haze (%) (m)
		Type (b) (k) (n)	Weight (%) (c)		
5					
10	AA	Nil	Nil	105	58
	AB	SA	0.35	121	38
15	19	SA A	(0.35) (0.89)	123	25
	AC	GA	0.35	122	35
20	20	GA A	(0.35) (0.8)	123	29
	AD	AA	0.35	121	35
25	21	AA A	(0.35) (0.72)	122	30
	AE	SUA	0.35	ND	39
30	22	SUA A	(0.35) (0.60)	ND	34
	AF	BA	0.35	123	56
35	23	BA A	(0.35) (0.86)	123	46
	AG	TA	0.35	ND	49
40	24	TA A	(0.35) (0.77)	ND	39
	AH	TBA	0.35	121	34
45	25	TBA A	(0.35) (0.59)	124	33

Notes to Table 5

- 50 (b) and (c) are both as defined in Notes to Table.
 (k), (l) and (m) are all as defined in Notes to Table 4.
 (n) SA is succinic acid.
 SUA is suberic acid.
 TA is toluic acid.
 55 ND means Not Determined.

Examples 26 to 28

The procedure described for Examples 11 to 18 was repeated with the exception that the polymer used was polymer I as defined in Note (a) in Notes to Table 1.

5 The results obtained are set out in Table 6.

Table 6

Example or Comp.Ex.	Additives		Cryst. temp.peak (°C) (l)	Haze (%) (m)
	Type (b) (k) (n)	Weight (%) (c)		
15 AI	N11	N11	116	77
AJ	GA	0.35	132	52
26	GA	(0.35)	133	48
20 A	A	(0.8)		
AK	SA	0.35	132	54
27	SA	(0.35)	135	41
25 A	A	(0.89)		
AL	BA	0.35	133	69
28	BA	(0.35)	135	47
30 A	A	(0.86)		

Notes to table 6

35

(b) and (c) are both as defined in Notes to Table 1.

(k), (l) and (m) are all as defined in Notes to Table 4.

(n) is as defined in Notes to Table 5.

40

Examples 29 to 36

The procedure described for Examples 11 to 18 was repeated using different amines and the random copolymer used in Examples 19 to 25.

45

The results obtained are set out in Table 7.

50

55

Table 7

	<u>Example or Comp.Ex.</u>	<u>Additives</u>		<u>Haze (%) (m)</u>	<u>Relative Clarity (p)</u>
		<u>Type</u>	<u>Weight</u>		
		<u>(b) (k) (n) (o)</u>	<u>(%) (c)</u>		
5					
10	AM	N11	N11	76	37
	AN	MHA	0.9	71	35
15	29	AA MHA	(0.35) (0.9)	31	150
	AO	AA	0.35	43	107
	AP	SA	0.35	42	115
20	30	SA MHA	(0.35) (0.9)	28	165
	AQ	GA	0.35	44	107
25	31	GA MHA	(0.35) (0.9)	29	160
	AR	DOA	0.35	66	35
30	32	GA DOA	(0.35) (0.5)	28	165
	AS	MCA	0.5	65	32
35	33	GA MCA	(0.35) (0.5)	30	175
40	34	GA MTA	(0.35) (0.5)	27	175
	AT	THD	0.5	62	37
45	35	GA THD	(0.35) (0.5)	29	165
	36	GA A	(0.35) (0.5)	29	165

50 Notes to Table 7

(b) and (c) are both as defined in Notes to Table 1.

(k) and (m) are both as defined in Notes to Table 4.

(n) is as defined in Notes to Table 5.

55 (o) HMA is an ethoxylated amine of the type $RR_1N(C_2H_4O)_nH$ where R_1 is methyl, n has a value of one and R is a mixture of linear and branched aliphatic groups containing from 13 to 15 carbon atoms.
DOA is an amine of the type RR_1R_2N where R is an octadecyl group and R_1 and R_2 are both methyl.

MCA is N-methyl-N,N-bis(coco)amine.

MTA is N,N-dimethyl-tallowamine.

THD is N-tallow-N,N'-tris(hydroxyethyl)-1,3-diaminopropane.

(p) Relative clarity is a comparison of the clarity of an injection moulded disc of the polymer compared to a standard. The apparatus consists of a light cabinet with a grid marked on the surface. 82.55mm (3.25 inches) above the top of the light cabinet is a flat support having a slit cut in it through which the grid is visible. The stand is surrounded by an enclosure with darkened interior surfaces.

Two reference discs are stacked together and placed over the slit to almost totally obscure the image of the grid as viewed through this pile of two discs. The test specimens (injection moulded discs obtained as described in Examples 11 to 22) are stacked over the slit, adjacent to the reference discs, further discs being added to the stack until the image of the grid viewed through the test specimens is almost totally obscured and corresponds essentially with the image seen through the reference discs. If exact correspondence is not achieved, an estimate of part discs is made.

The relative clarity is expressed as the number of discs in the stack multiplied by 10, that is a relative clarity of 100 corresponds to a stack of 10 discs.

Examples 37 to 43

Masterbatch compositions were prepared using either an acid or an amine.

The masterbatches were prepared using the random propylene copolymer of Examples 19 to 25 and contained either 5% by weight of additive (adipic acid or glutaric acid) or 10% by weight of additive (succinic acid or the ethoxylated amine $RN(C_2H_4OH)_2$ where R is a mixture of linear and branched aliphatic groups containing from 13 to 15 carbon atoms). The masterbatches were prepared on a Polymix 150 type two roll mill (available from Schwabenthan) with the front roll at 190°C and the rear roll at 150°C. The molten polymer was granulated using a Pallmann type PS/2 granulator.

Portions of the masterbatches thus obtained were added to a further quantity of the same random propylene copolymer in amounts to give the desired final level of acid, or acids, and amine, as set out in Table 8. The masterbatches were tumble blended with the polymer and the mixture thus obtained was extruded, granulated and finally injection molded as in Examples 11 to 18. Injection moulded samples were also prepared by tumble blending masterbatches and polymer and injection moulding the mixture with no extrusion and granulating stages.

The compositions produced and the results obtained are set out in Table 8.

Table 8

	<u>Example or Comp. Ex.</u>	<u>Additives</u>		<u>Relative Clarity (p) (r)</u>
		<u>Type</u> (b) (k) (n) (q)	<u>Weight</u> (%) (c)	
5				
10	37	AA SA A	(0.30) (0.085) (0.15)	127
15	38	AA SA A	(0.30) (0.085) (0.15)	145*
20	39	AA* SA* A	(0.30) (0.085) (0.15)	137
25	40	AA* SA* A	(0.30) (0.085) (0.15)	165*
30	AU	AA SA	(0.30) (0.085)	105
35	41	AA A	(0.30) (0.15)	122
40	AV	AA	0.30	102
	AW	GA	0.35	130
	42	GA A	(0.35) (0.15)	145
	43	GA A	(0.35) (0.50)	160

Notes to Table 8

(b) and (c) are both as defined in Notes to Table 1.

45 (k) is as defined in Notes to Table 4.

(n) is as defined in Notes to Table 5.

(p) is as defined in Notes to Table 7.

(q) * These components were added as powders and had not been preformed into a masterbatch.

50 (r) * These results were obtained using moulded discs obtained by tumble blending polymer and additives (either as masterbatch or powder) and injection moulding the blended mixture without prior extrusion and granulation stages.

Examples 44 to 49

55

The procedure described for Examples 11 to 18 was repeated using various mixtures of acids and amines and also various preformed reaction products of the acids and amines.

The materials used, and the results obtained, are set out in Table 9.

Table 9

	<u>Example or Comp.Ex.</u>	<u>Additives</u>		<u>Haze (%) (m)</u>	<u>Relative Clarity (p)</u>
		<u>Type (b) (o) (s)</u>	<u>Weight (%) (c)</u>		
5					
10	AX	Nil	Nil	76	20
	44	AA HMA	(0.35) (0.70)	48	90
15	45	AA HMA	(0.35) (0.90)	46	97
	AY	RP 1	1.00	73	42
20	AA	RP 2	1.65	78	25
	BA	RP 3	1.87	74	25
	BB	RP 4	1.12	70	27
25	BC	RP 5	0.72	64	55
	46	AA A	(0.35) (0.50)	ND	120
30	47	AA A	(0.35) (0.70)	ND	125
	48	AA A	(0.35) (0.90)	ND	125
35	49	AA A	(0.35) (1.8)	ND	130

Notes to Table 9

(b) and (c) are both as defined in Notes to Table 1.

(m) is as defined in Notes to Table 4.

(o) and (p) are both as defined in Notes to Table 7.

(s) Each RP is a reaction product of an adipic acid and an amine obtained by stirring the acid and amine together, heating the mixture, under nitrogen, to 240°C and maintaining at 240°C for two hours. Reaction appeared to proceed quickly and to be essentially complete in 30 minutes.

RP 1 is the reaction product of AA and HMA in a molar ratio of 1:1.

RP 2 is the reaction product of AA and HMA in a molar ratio of 1:2.

RP 3 is the reaction product of AA and A in a molar ratio of 1:2.

RP 4 is the reaction product of AA and A in a molar ratio of 1:1.

RP 5 is the reaction product of AA and A in a molar ratio of 2:1.

Each RP material was used in an amount corresponding to 0.35% by weight of adipic acid. The products obtained were esters and in the case of RP 1 some amide was also found to be present but amide was not detected in the other products.

Claims

1. A composition comprising
 - (a) a carboxylic acid compound which contains at least three carbon atoms; and
 - (b) an amine.
2. A composition as claimed in claim 1 wherein the carboxylic acid compound contains at least two carboxylic acid groups attached to a saturated aliphatic hydrocarbon group and is selected from glutaric acid, adipic acid, succinic acid or suberic acid.
3. A composition as claimed in claim 1 wherein the carboxylic acid contains at least one carboxylic acid group attached to a ring system and is selected from benzoic acid, p-tertiary butyl benzoic acid, cyclohexane-1,2-dicarboxylic acid and cyclohexane-1,4-dicarboxylic acid.
4. A composition as claimed in any one of claims 1 to 3 wherein the amine is a compound of general formula I or II:

$$\begin{array}{ccc} \text{RN} & - (\text{CH}_2)_m & - \text{NR} \\ | & & | \\ \text{R}_1 & & \text{R}_1 \end{array} \quad \text{I}$$

$$\text{RR}_1\text{R}_2\text{N} \quad \text{II}$$
- wherein:
 - R is a hydrocarbyl group or a substituted hydrocarbyl group;
 - R₁ is a hydrocarbyl group, a substituted hydrocarbyl group or a group (R₃O)_x(C₂H₄O)_nH;
 - R₂ is a hydrocarbyl group, a substituted hydrocarbyl group or a group (R₃O)_x(C₂H₄O)_nH, and may be the same as, or different from R₁;
 - R₃ is an alkylene group containing 3 to 5 carbon atoms;
 - m is an integer and has a value of 1 to 10;
 - n is zero or is an integer which has a value of from 1 to 50;
 - and
 - x is zero or is an integer which has a value of from 1 to 50.
5. A composition as claimed in any one of claims 1 to 4 wherein the amine contains at least one group which is an alkyl group, or is a mixture of alkyl groups, containing from 8 to 20 carbon atoms.
6. A composition as claimed in claim 5 wherein the amine is
 - N,N-bis(hydroxyethyl)-alkyl(C₈ to C₁₈)amine;
 - N-methyl-N-hydroxyethyl-alkyl(C₈ to C₁₈)amine;
 - N,N-dimethyl-octadecylamine;
 - N,N-bis(hydroxyethyl)-octadecylamine;
 - N-methyl-N,N-bis(coco)amine;
 - N,N-dimethyl-tallowamine; or
 - N-tallow-N,N',N'-tris(hydroxyethyl)-1,3-diaminopropane.
7. A composition as claimed in any one of claims 1 to 6 wherein (a) and (b) are in the molar proportions from 10:1 to 1:10.
8. A polymer composition comprising an olefin polymer and a composition as claimed in any one of claims 1 to 7.
9. A polymer composition as claimed in claim 8 which contains from 0.05% up to 50%, by weight, relative to the polymer of the composition claimed in any one of claims 1 to 7.
10. A polymer composition as claimed in claim 9 wherein the proportion of the carboxylic acid compound is from 0.05% up to 3% by weight, relative to the polymer and the proportion of the amine is from 0.05 up to 3% by weight, relative to the polymer.
11. A shaped article obtained by injection moulding a polymer composition as claimed in any one of claims 8 to 10.

12. A process for the production of a polymer composition which comprises blending an olefin polymer with a carboxylic acid compound which contains at least three carbon atoms and with an amine, or with a mixture of a carboxylic acid compound which contains at least three carbon atoms and an amine wherein the acid and the amine are together subjected to an elevated temperature only once.

5 13. A process as claimed in claim 12 wherein the acid and amine are added separately to the polymer during an injection moulding stage.

10

15

20

25

30

35

40

45

50

55

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 267 695
A3**

12

EUROPEAN PATENT APPLICATION

21 Application number: 87309135.9

51 Int. Cl.4: C08K 5/00 , C08L 23/02 ,
//(C08K5/00,5:09,5:17)

22 Date of filing: 15.10.87

30 Priority: 11.11.86 GB 8626875
23.01.87 GB 8701514

43 Date of publication of application:
18.05.88 Bulletin 88/20

64 Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SE

68 Date of deferred publication of the search report:
20.09.89 Bulletin 89/38

71 Applicant: IMPERIAL CHEMICAL INDUSTRIES
PLC
Imperial Chemical House Millbank
London SW1P 3JF(GB)

72 Inventor: Trotoir, Jean-Paul
236 rue des Bruyères
B-5043 Waret-la-Chaussée(BE)
Inventor: Bath, Colin
1 East View Summerseat
Bury Lancashire BL9 5PG(GB)

74 Representative: James, David Gomer et al
Imperial Chemical Industries PLC Legal
Department: Patents Po Box 6 Bessemer
Road
Welwyn Garden City Herts, AL7 1HD(GB)

54 Composition comprising a carboxylic acid and an amine.

57 A composition comprises (a) a carboxylic acid compound which contains at least three carbon atoms and (b) an amine such as an ethoxylated amine. The composition may be obtained by conventional powder blending or melt blending techniques. The composition can be incorporated into an olefin polymer to give a polymer composition which has an increased crystallisation temperature and/or improved optical properties.

EP 0 267 695 A3



EP 87 30 9135

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	CHEMICAL ABSTRACTS, vol. 107, no. 68, 1987, page 425, abstract no. 65582p, Columbus, Ohio, US; S. KOPACZ et al.: "Separation of cobalt(II) from sulfate solutions by using mixtures of benzoic and o-toluic acids with 3,4-dimethylaniline in benzene", & CHEM. ANAL. (WARSAW) 1986, 31(4), 645-51 * Abstract * ---	1	C 08 K 5/00 C 08 L 23/02 // (C 08 K 5/00 C 08 K 5:09 C 08 K 5:17)
X	FR-A-2 318 720 (TBA INDUSTRIAL PRODUCTS LTD) * Claims 1-3,9-11; table 1 * ---	8-10,12	
A	PLASTICS ENGINEERING, vol. 42, no. 8, August 1986, pages 41-44, Brookfield Center, CT, US; L.E. WALP et al.: "Antistats for polyolefins: Check out ethoxylates" * Pages 42-45 * -----	4-6	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 08 K C 08 L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 27-06-1989	Examiner WILSON A.J.D.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	